

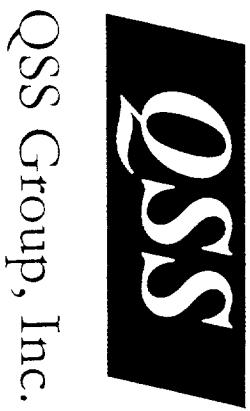
Characterization of C/SiC Ceramic Matrix Composites (CMCs) with Novel Interface Fiber Coatings

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Abstract

Ceramic Matrix Composites (CMCs) are attractive candidate materials in the aerospace industry due to their high specific strength, low density and higher temperature capabilities. The National Aeronautics and Space Administration (NASA) is pursuing the use of CMC components in advanced Reusable Launch Vehicle (RLV) propulsion applications. Carbon fiber-reinforced silicon carbide (C/SiC) is the primary material of interest for a variety of RLV propulsion applications. These composites offer high-strength carbon fibers and a high modulus, oxidation-resistant matrix. For comparison, two types of carbon fibers were processed with novel types of interface coatings (multilayer and pseudoporous). For RLV propulsion applications, environmental durability will be critical. The coatings show promise of protecting the carbon fibers from the oxidizing environment. The strengths and microstructures of these composite materials are presented.



Characterization of C/SiC Ceramic Matrix Composites with Novel Fiber Coatings

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Key Words: Composites, Carbon Fiber, Ceramic Matrix Composites

Introduction

NASA is pursuing the use of Ceramic Matrix Composites (CMCs) in 3rd Generation Reusable Launch Vehicle propulsion applications.

- CMC's are being developed to provide significant increases in safety and engine performance while reducing costs.
- Carbon fiber-reinforced silicon carbide matrix (C/SiC) composites are the current focus.
- Properties of C/SiC composites can be modified by changing the fiber, the interface, and/or the ceramic matrix. Surface coatings can also be applied to improve the durability.

Objective

- To correlate the mechanical behavior of different types of C/SiC materials with composite microstructure in order to assess the suitability of these materials for further development.

- Safety gains can be realized through the use of durable CMC components having higher specific strength and increased temperature margins.
- The identification of an ideal fiber-interface-matrix-surface coating system yielding improved environmental durability is critical to the development and application of advanced composite materials.

Background: Properties and Microstructure of Typical CVI C/SiC

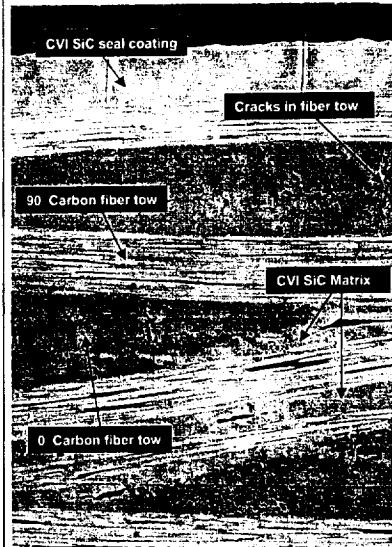
Mechanical, Physical, and Thermal Properties of Current 2D CVI C/SiC

Property (Units)	Value
RT Tensile Strength (ksi)	75
2200 °F Tensile Strength (ksi)	79
Interlaminar Shear (ksi)	5.0
Density (g/cc)	2.05
RT Thermal Conductivity (Btu/hr·ft·°F)	3.8

- Utilizes T-300 fiber
- Plain weave (PW) fabric
- Pyrolytic carbon (PyC) interface
- 45 v/o fiber

Source: Honeywell Advanced Composites, Inc.

Microstructure of 2D CVI C/SiC



- C/SiC composites exhibit the highest specific strength of current advanced materials over a wide temperature range, and are thus being evaluated for high temperature applications.
- Processing of C/SiC composites produces microcracks in the CVI SiC seal coating, the SiC matrix, and within the fiber tows.
- 0° fiber tows run parallel to the load direction; 90° fiber tows run perpendicular to the load direction.

Environmental Durability is Essential for Space Propulsion Applications

Factors Influencing the Degradation of C/SiC

- Matrix microcracks present in as-processed material
- Operating conditions—Component may be subjected to high pressure/velocity gas (O₂, H₂O, H₂ could be present), a wide range of temperatures, and high stress
- Oxidation of interfaces and fibers
- Volatilization of protective oxide (silica)
- Foreign object damage (FOD)
- Matrix/seal coat spalling
- Thermal shock
- Desire to operate engine system several hundred missions without refurbishment

• Microcracks allow the ingress of oxygen to the carbon fibers. Oxidation of the fibers will then begin to take place, which leads to reductions in strength and durability.

• Gen 3/Hypersonics goals require that these materials have the ability survive hundreds of hours of operation.

Means of Preventing of Fiber/Interface Oxidation in C/SiC

- Oxidation-resistant interfaces
- Matrix-oxidation inhibitors
- Surface coatings

- In this study we are looking at oxidation-resistant interfaces to prevent or delay oxidation of the carbon fibers.
- Future work will include evaluating surface coatings applied to the materials characterized in this study. A carbon-boron-silicon surface coating will be applied to tensile specimens to assess its role in improving environmental durability.

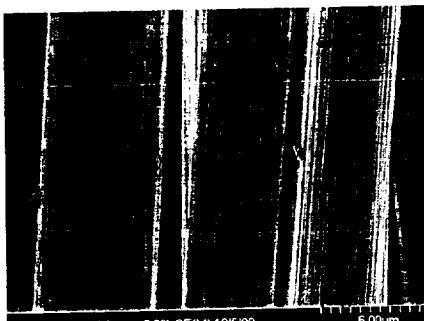
C/SiC Materials Examined

Supplier	C Fiber	Matrix	Interface (Fiber Coating)
Honeywell ACI	T-300 (1K)	CVI SiC	PyC Coating
Honeywell ACI	T-300 (1K)	CVI/MI SiC	PyC Coating
Hyper-Therm, Inc.	T-300 (3K)	CVI SiC	Multilayer Coating (SiC and C)
Hyper-Therm, Inc.	T-300 (3K)	CVI SiC	Pseudo-Porous Coating (SiC and C)
Hyper-Therm, Inc.	IM7 (6K)	CVI SiC	Multilayer Coating (SiC and C)
Hyper-Therm, Inc.	IM7 (6K)	CVI SiC	Pseudo-Porous Coating (SiC and C)

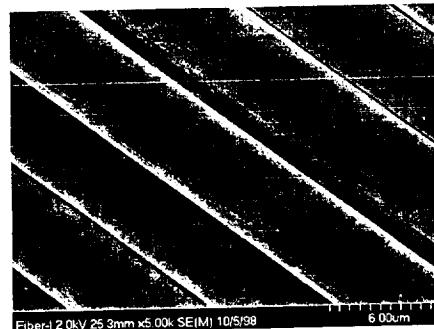
- All 2D [0/90] layups.
- All tensile samples (6 x 0.5 in.) were CVI SiC seal coated.

- The Honeywell materials with the PyC coating exhibit good fiber-matrix debonding and high room temperature strength, but oxidation of the fibers and interface limits life (Ref. 2).
- This was the first attempt by Hyper-Therm, Inc. to deposit multilayer and pseudo-porous interface coatings on carbon fibers. These were evaluated as alternatives to the typical pyrolytic carbon interfaces.

Carbon Fibers



T-300



IM7

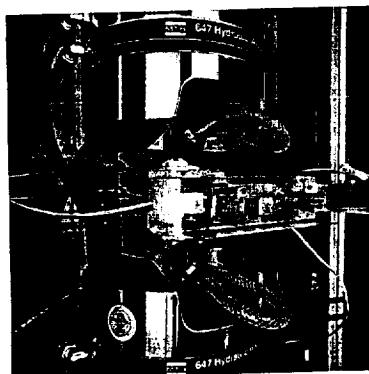
Carbon Fiber	Tensile Modulus (Msi)	Tensile Strength (ksi)	Tow Count (fibers/tow)	Fiber Surface
T-300	33.4	512	1K, 3K	Crenulated
IM7	40	780	6K	Smooth

(Ref. 1)

- Looking at the surfaces of these fibers, one can see how they vary. The room temperature tensile strength and modulus of the IM7 fibers are noticeably higher than those of the T-300 fibers.
- Uniform deposition of the interface within fiber tows should be easier with smaller tows such as the 1K tow size. Also, with the smaller tows, the surface of the composite is smoother. When weaving fabric (plain weave for example), the smaller the tow size, the smaller the crimp angle would be, which reduces stress on the fibers.
- The 3K tows are easier to weave and braid.
- The IM7 fibers were only available in 6K or 12K tow size.

Testing

- Room temperature tensile testing
- Tensile stress-rupture tests ($\sigma = 10$ ksi) were performed at 2200 °F (1200 °C) in air (1 atm) as screening tests to assess relative durability of the composites in oxidizing environments



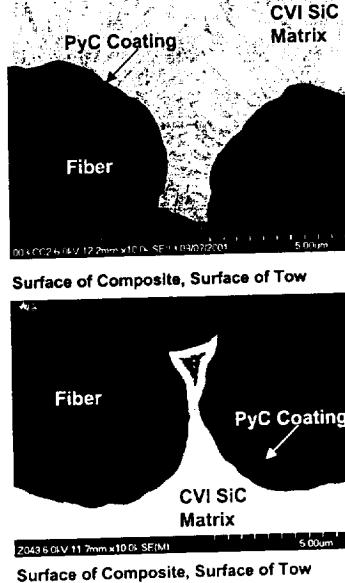
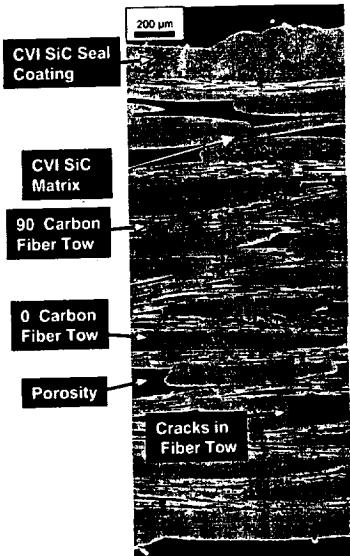
Microstructural Characterization

Examined:

- Polished sections of as-manufactured C/SiC specimens —*emphasis on examining interface (nature of coating and uniformity)*
- Polished sections of stress-rupture test specimens—*emphasis on examining degradation within the gage section in order to identify damage mechanisms*
- Fracture surfaces of room temperature tensile test specimens—*emphasis on correlating mechanical properties with microstructure*

- Examination of the fracture surfaces is in progress.

C/SiC: T-300 (1K) Fiber, CVI SiC Matrix, Pyrolytic Carbon (PyC) Coating

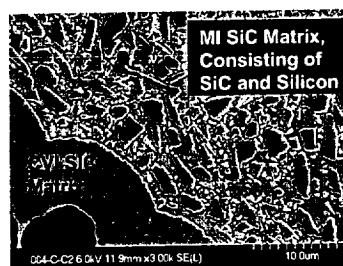
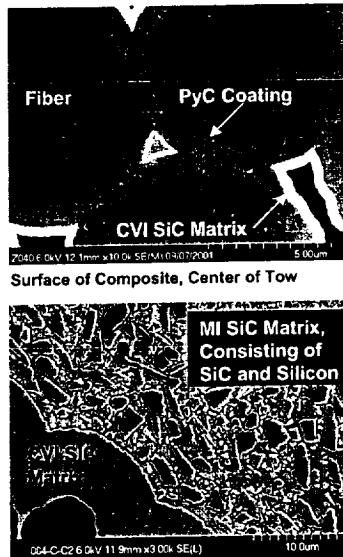
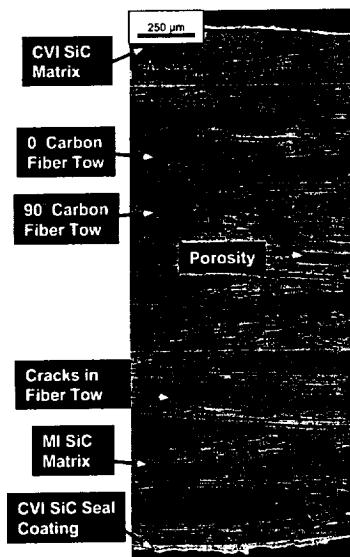


Fiber Coating: Typical PyC C/SiC interface. Fiber coating ranged from 0.7 - 0.8 μm throughout the specimen.

Fiber Loading: 47 v/o
Density: 2.03 g/cm³
RT Strength: 66 ksi
Ult. Strain: 0.96%

- The as-processed Honeywell CVI composite shows regions of interlaminar porosity and microcracking throughout the sample.
- At higher magnification, one can see that the PyC coating around the fibers is very uniform.

C/SiC: T-300 (1K) Fiber, CVI MI/SiC Matrix, Pyrolytic Carbon (PyC) Coating



Fiber Coating: PyC coating. Typical C/SiC interface. Fiber coating ranged from 0.7-0.8 μm throughout the specimen.

Fiber Loading: 47 v/o

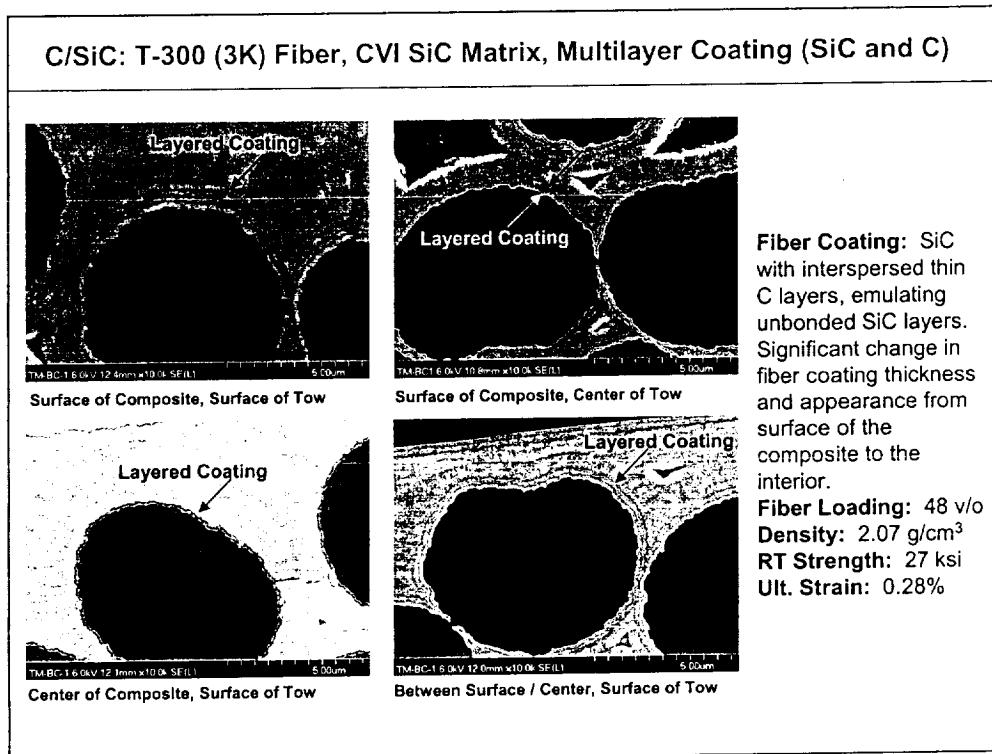
Density: 2.07 g/cm³.

Melt infiltrated matrix (silicon/SiC particles) reduces porosity level.

RT Strength: 62 ksi

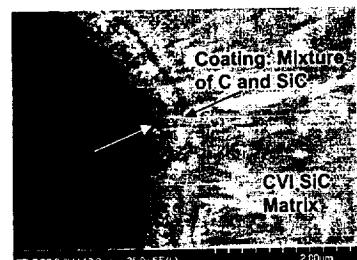
Ult. Strain: 0.78%

- The as-processed Honeywell MI (melt infiltrated) composite had a slightly higher density than the CVI composite, and exhibited a reduced amount of porosity.
- There still are microcracks present throughout the sample.
- The PyC coating is very uniform around the fibers.

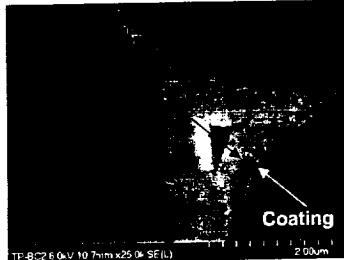


- There are changes in fiber coating thickness and appearance from the surface of the composite to the interior. Very thin fiber coatings were observed in the center of the composite.
- Improving the uniformity of the fiber coating could improve the mechanical properties.

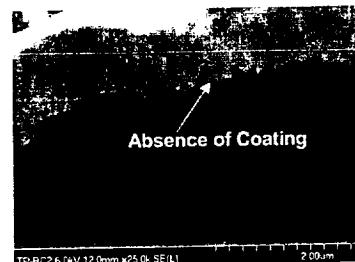
C/SiC: T-300 (3K) Fiber, CVI SiC Matrix, Pseudo-Porous Coating (SiC/C)



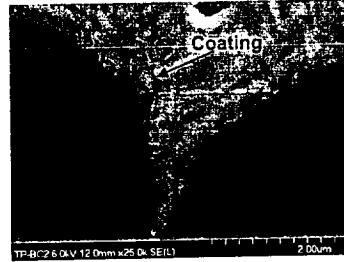
Surface of Composite, Surface of Tow



Surface of Composite, Center of Tow



Center of Composite, Surface of Tow



Between Surface / Center, Surface of Tow

Fiber Coating: SiC and C are co-deposited. The C is supposed to emulate porosity. C-rich portion of the fiber coating: fairly uniform to a depth of 1/4 the sample thickness.

Fiber Loading: 46 v/o

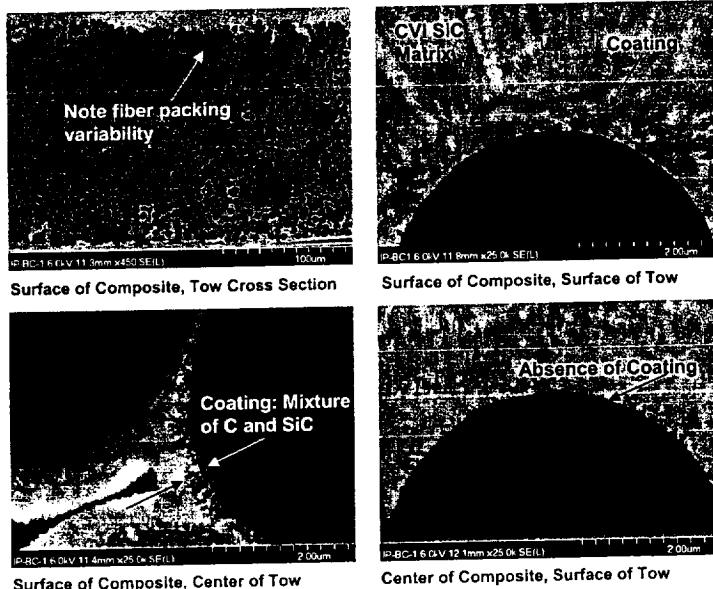
Density: 1.96 g/cm³

RT Strength: 28 ksi

Ult. Strain: 0.33%

- The fiber coating varied within the sample. Coatings were fairly uniform in the outer portions of the sample. The coating appearance varies from the surface, to the center of the tow. Towards the center of the sample, there is an absence of the coating.
- Improving the uniformity of the fiber coating could improve the mechanical properties.

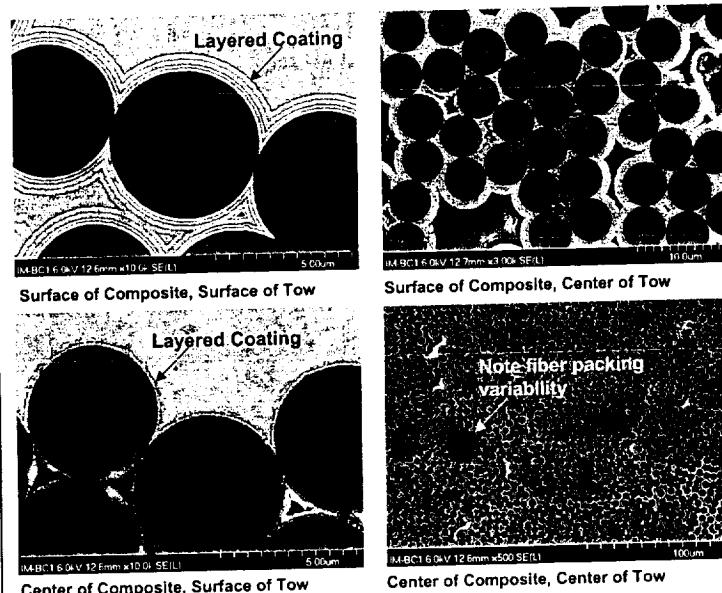
C/SiC: IM7 (6K) Fiber, CVI SiC Matrix, Pseudo-Porous Coating (SiC/C)



Fiber Coating: SiC and C are co-deposited. The C is supposed to emulate porosity.
Coating: less distinct than pseudo-porous coating on T-300 fibers.
Fiber Loading: 43 v/o
Tows are quite large, and fiber packing within the tows is variable.
Density: 1.99 g/cm³
RT Strength: 25 ksi
Ult. Strain: 0.23%

- The coating is less distinct than the pseudo-porous coating on the T-300 fibers. Towards the center of the composite, there is an absence of coating.
- The 6K tows are quite large and fiber packing within the tows is variable. It is difficult to deposit coatings uniformly throughout such large tows.

C/SiC: IM7 (6K) Fiber, CVI SiC Matrix, Multilayer Coating (SiC and C)



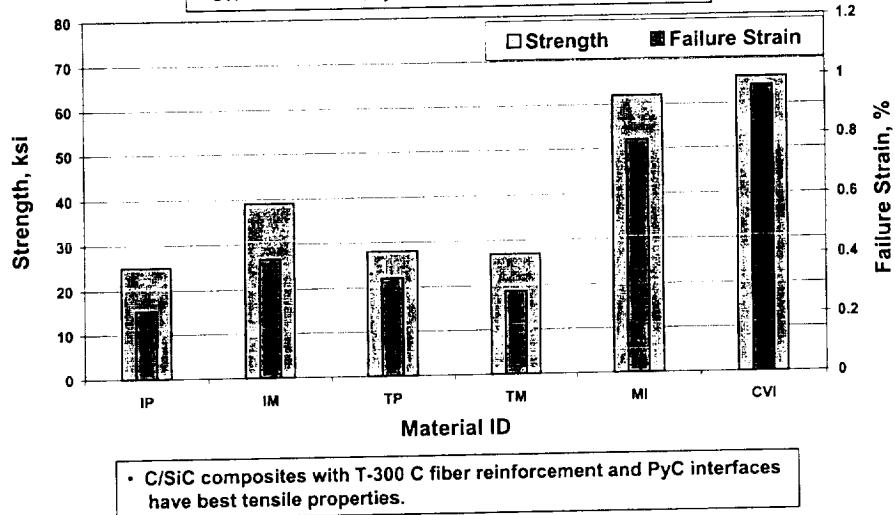
Fiber Coating: SiC with interspersed thin C layers, emulating unbonded SiC layers. Significant change in fiber coating thickness and appearance from surface of the composite to the interior.

Fiber Loading: 44 v/o
Density: 1.97 g/cm³
RT Strength: 39 ksi
Ult. Strain: 0.40%

- Due to the size of the large fiber tows and the close packing of the IM7 fibers, the coating layers are nonuniform as one moves toward the center of the tow. The fiber coating thickness and appearance change as one moves toward the center of the composite.
- Improving the uniformity of the fiber coating could improve the strength.

Room Temperature Tensile Properties of Different C/SiC Materials

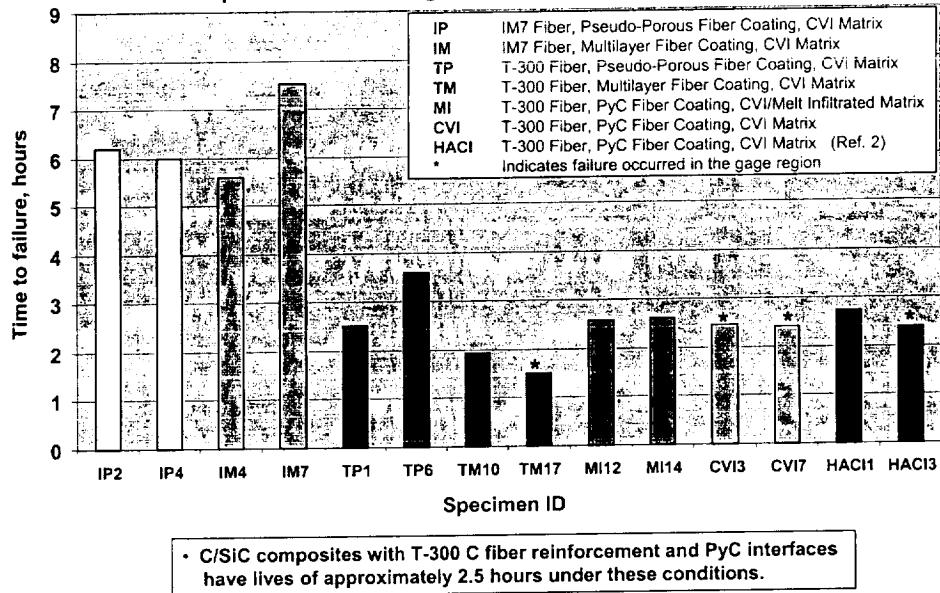
IP	IM7 Fiber, Pseudo-Porous Fiber Coating, CVI Matrix
IM	IM7 Fiber, Multilayer Fiber Coating, CVI Matrix
TP	T-300 Fiber, Pseudo-Porous Fiber Coating, CVI Matrix
TM	T-300 Fiber, Multilayer Fiber Coating, CVI Matrix
MI	T-300 Fiber, PyC Fiber Coating, CVI/Melt Infiltrated Matrix
CVI	T-300 Fiber, PyC Fiber Coating, CVI Matrix



- At room temperature, the Honeywell MI and CVI materials exhibited the best strength. This is preliminary data, and more data points for Hyper-Therm, Inc. IP, IM, TP, and TM will be included in future work.

**Stress-Rupture Lives of Different C/SiC Materials
(1200°C, 10 ksi in air)**

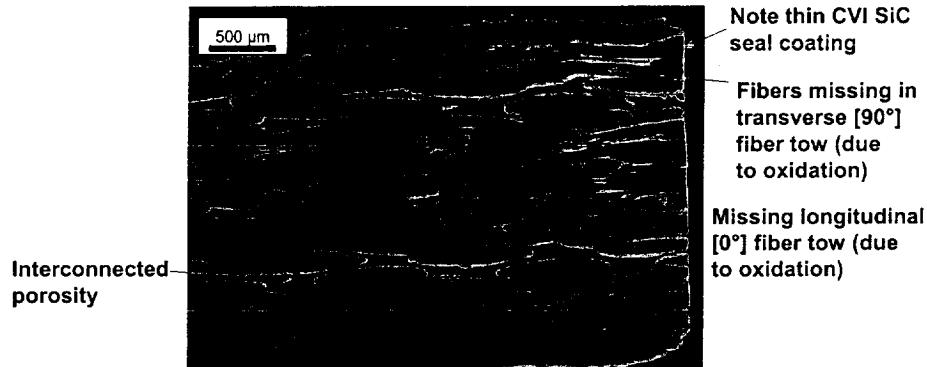
C/SiC composites containing IM7 fibers exhibited the longest lives



- Composites utilizing the IM7 fiber exhibited the longest lives. Under these conditions, the IM7 composites last approximately twice as long as the composites with PyC interfaces and T-300 fiber reinforcement (MI, CVI, and HACI).
- Results from this study (MI and CVI) are consistent with those obtained previously (HACI).

C/SiC Stress-Rupture Tested at 2200 °F (1200 °C) in Air ($\sigma = 10$ ksi)

C/SiC: T-300 (1K) Fiber, CVI SiC Matrix, Pyrolytic Carbon (PyC) Coating



Polished Cross Section of Tensile/Creep Specimen, Center of Gage Section

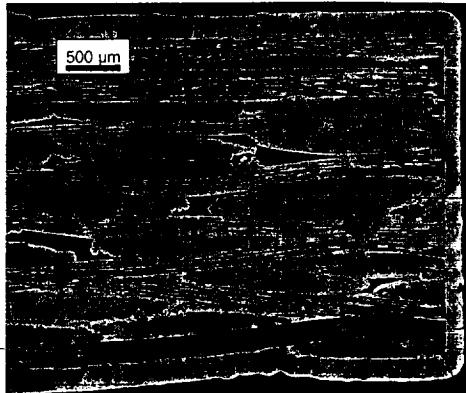
- Specimen failed after 2.5 hours of testing. Failure occurred in the gage section.
- Oxidation of carbon fibers and interfaces during creep loading is the primary damage mechanism observed in the gage section.

• Oxidation of the carbon fibers has occurred on the outside (machined) edge of the composite near the thin CVI seal SiC coating. This indicates the need for improved means of protecting carbon fibers from oxidation.

C/SiC Stress-Rupture Tested at 2200 °F (1200 °C) in Air ($\sigma = 10$ ksi)

IM7 (6K) Fiber, CVI SiC Matrix, Pseudo-Porous Coating (SiC/C)

Missing transverse
[90°] fiber tow (due
to oxidation)



Crack in CVI SiC
seal coating

Missing longitudinal
[0°] fiber tow (due
to oxidation)

Polished Cross Section of Tensile/Creep Specimen, Center of Gage Section

- Specimen failed after 6.2 hours of testing. Failure occurred 1.5 in. from end of specimen .
- Oxidation of carbon fibers during creep loading is the primary damage mechanism observed in the gage section.

- Oxidation of the carbon fibers occurred on the outside edge of the composite. Cracks in the seal coat allowed oxygen ingress and fiber damage.
- Failure occurred outside the gage section.

Summary and Conclusions

- Six C/SiC composites comprising different ceramic matrices, fibers, and interfaces are currently being evaluated. Initial microstructural characterization and mechanical property results have been obtained.
- C/SiC CMCs with PyC fiber coatings and T-300 C fiber reinforcement exhibited the highest room temperature strength.
- The C/SiC CMCs reinforced with T-300 fibers exhibited very similar "time to failure" behavior in stressed oxidation tensile tests, even though they comprised different matrices (MI and CVI) or interfaces (PyC, multilayer, or pseudo-porous).
- Developmental C/SiC materials reinforced with IM7 fiber exhibited better durability in stressed oxidation tests in spite of interface (fiber coating) nonuniformity and lower room temperature strengths/strain to failure.

Future Work

- Fractography of RT tensile and 1200°C stressed oxidation specimens is in progress.
- The examination of the fracture surfaces and the behavior of the novel interfaces will help guide material development.
- Specimens coated with the GEPSC (General Electric Power Systems Composites) cbs (carbon-boron-silicon) coating are being tested at 1200°C under 10 ksi.
- CVI C/SiC specimens with IM7 (6K) fibers and PyC interfaces will be fabricated and tested.
- Improving the uniformity of the novel fiber coatings and/or modifying their composition could improve the mechanical properties of this CMC.

References

1. Cape Composites, Inc.: Carbon Fiber Data Sheet
2. Michael Verrilli, J. Douglas Kiser, Elizabeth Opila, and Anthony Calomino, "Effect of Environment on Stress-Rupture Behavior of a Carbon Fiber- Reinforced Silicon Carbide (C/SiC) Ceramic Matrix Composite," Proceedings of the National Space and Missile Materials Symposium, Monterey, CA, June 24-28, 2001.